Processing of Cellulose-Ionic Liquid Solutions to Produce Beads with Specific and Controllable Properties

James Coombs OBrien, Janet L. Scott, Davide Mattia, Laura Torrente Murciano, Paul Murray

Doctoral Training Centre, Centre for Sustainable Chemical Technologies, University of Bath, BA2 7AY, UK.

e-mail: j.coombs.obrien@bath.ac.uk, URL:http://www.bath.ac.uk/csct

Cellulose Dissolution

An estimated 1.5 × 10^{12} tons of cellulose is generated every year making it the most abundant biopolymer on the planet.[1] However, the wide scale sustainable use of this almost inexhaustible raw material is hindered by its low solubility by virtue of an extensive hydrogen bonding network (*Figure 1, **A***).

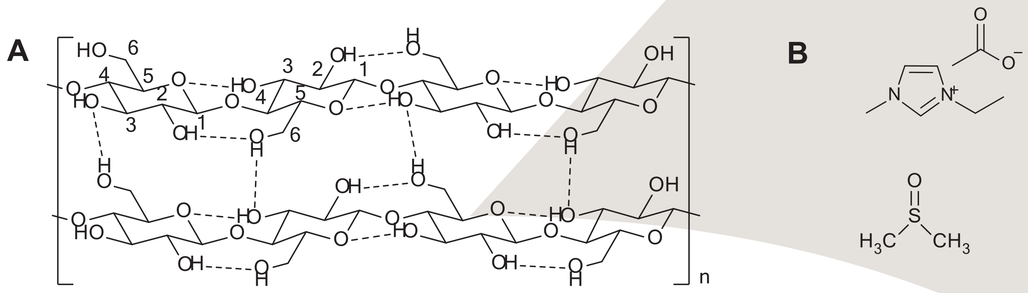
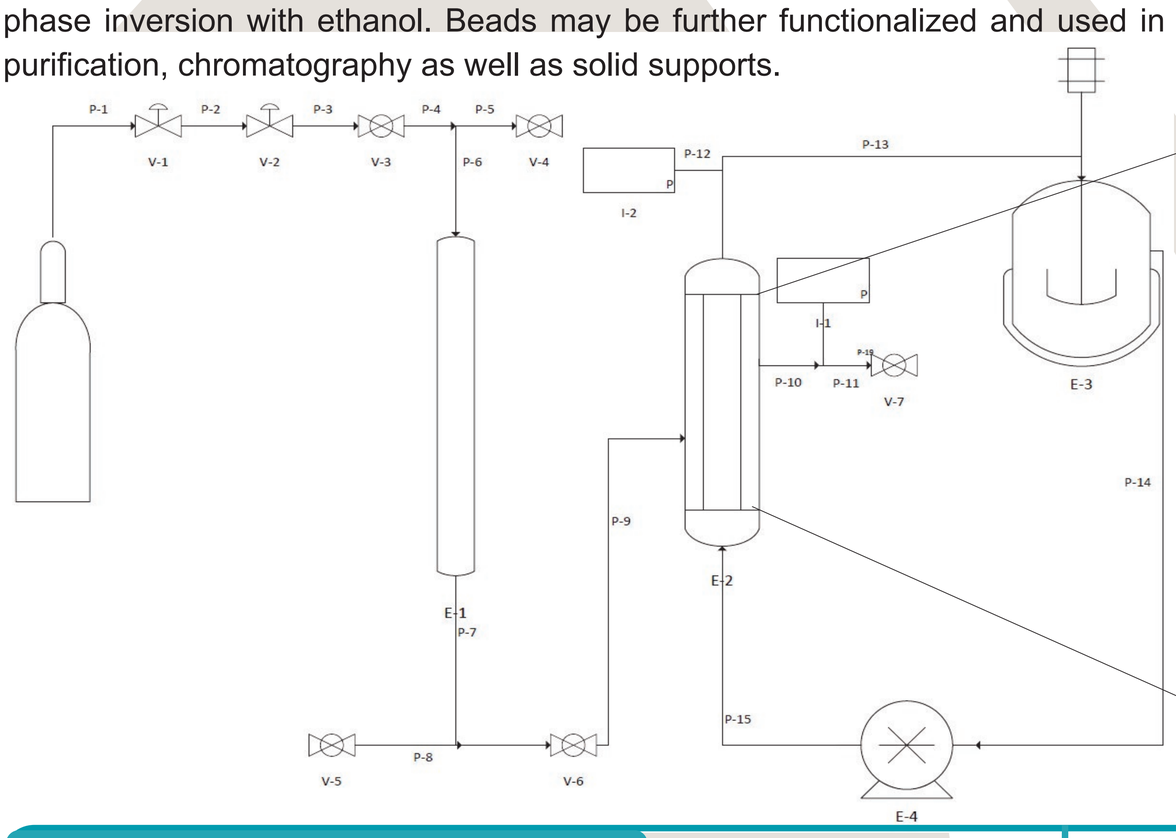


*Figure 1: **A** = Diagram of the inter and intra-chain bonding of cellulose.[2,3]*

***B** = The ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMOAc) and co-solvent DMSO.*

Ionic liquids (ILs) can dissolve cellulose opening up a potential processing avenue especially when used with a co-solvent, such as DMSO, due to reduced viscosity, faster dissolution and less ionic liquid.[4, 5]

Here we demonstrate the controlled formation of cellulose beads by membrane emulsification of solutions of cellulose dissolved in EMIMOAc-DMSO (*Figure 1*, **B**) followed by phase inversion with ethanol. Beads may be further functionalized and used in water purification, chromatography as well as solid supports.



Membrane Emulsification

Emulsions, a mixture of two immiscible liquids, are usually formed via high shear force processes. There is, however, a drive towards lower energy and less harsh membrane emulsification techniques which also provide greater control over dispersity and droplet size (*Figure 2*).

Water in Oil emulsions (W/O), stabilised with a surfactant, were used as a precursor to cellulose bead products. Specifically, cellulose solutions were dispersed in a continuous sunflower oil phase then subject to an anti-solvent producing solid cellulose beads (*Figure 3*).

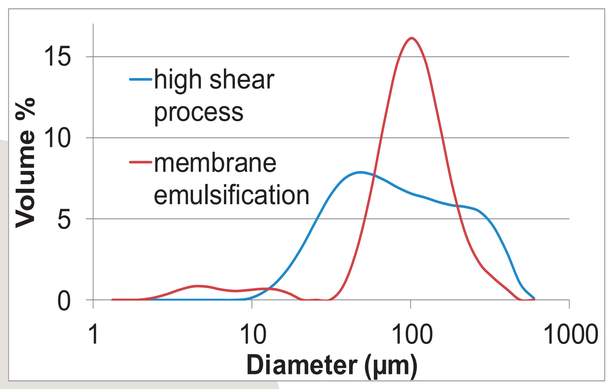
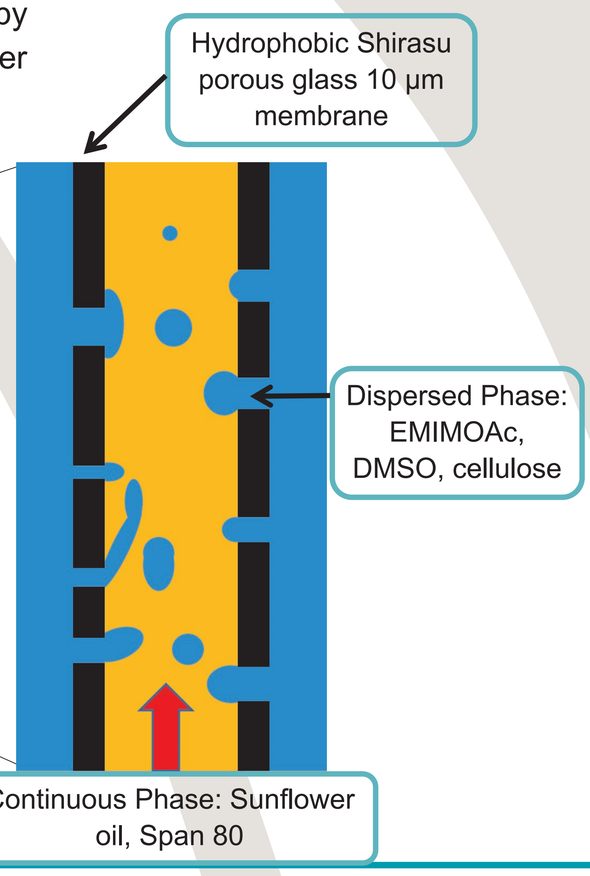


Figure 2: A comparison between the particle size distribution of cellulose beads made via two different techniques.

Control of polydispersity and particle size is important and influenced by a range of factors including: **temperature, flow rate, surfactant concentration, cellulose concentration, membrane pore size** etc. These factors influence the beads via changes in the viscosity and interfacial tension.



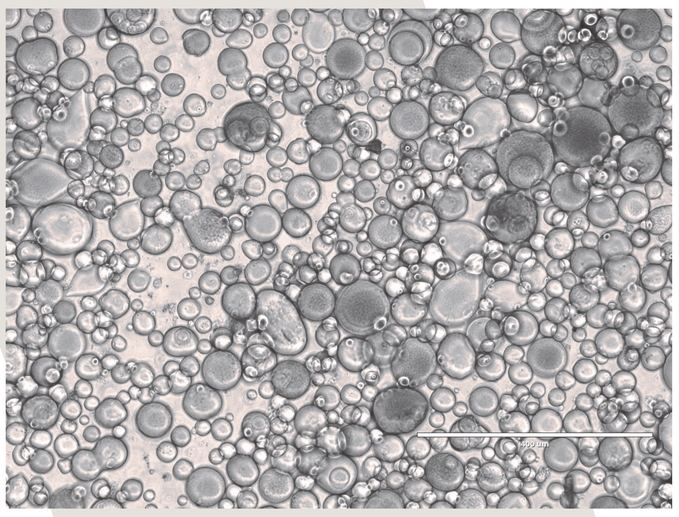


Figure 3: Optical Micrograph of cellulose beads—scale bar = 400µm.

Design of Experiments

An experimental design approach enabled a wide coverage of processing parameters in relatively few experiments.

Interfacial tension influences particle size. In this system it was found that this parameter is controlled by the temperature and surfactant concentration (*Figure 4*).

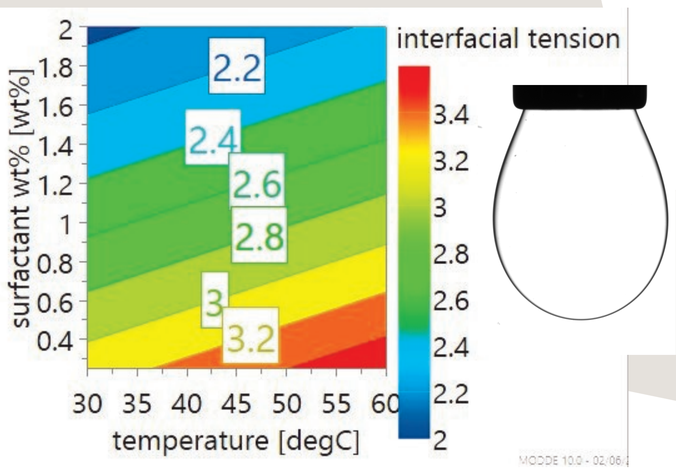
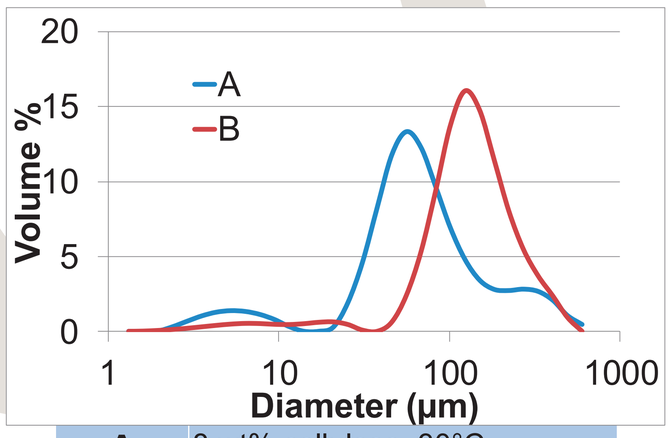


Figure 4: Graph showing the influence of surfactant wt%(Span 80) and temperature on the interfacial tension of emulsions of cellulose solutions suspended in sunflower oil.

Whilst maintaining the same membrane pore size (10 µm) it was possible to change the size and size distribution of the final product by adjusting the process parameters: **surfactant concentration, temperature, cellulose amount and flow rate** (*Figure 5* and 6).



A	8 wt% cellulose, 30°C, 0.25wt% Span 80, 2.4Lmin^{-1}
B	4 wt% cellulose, 30°C, 0.25wt% Span 80, 0.4Lmin^{-1}

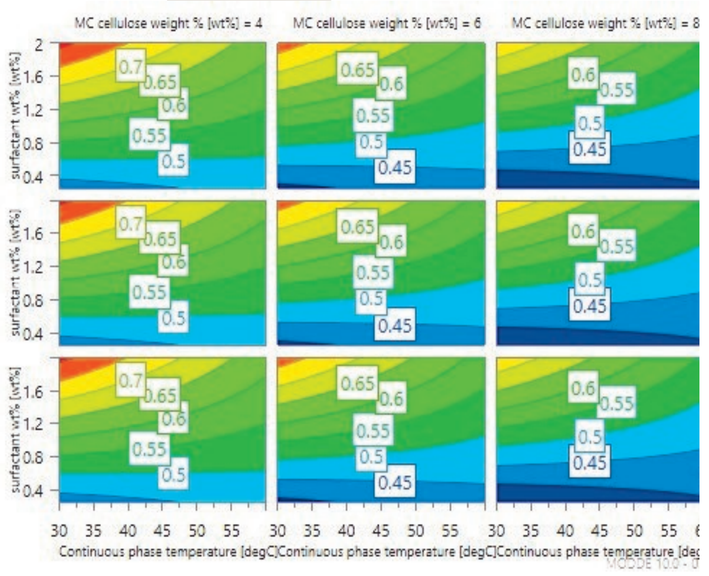


Figure 5: Influence of process parameters on particle size (left) and size distributions (right).

References

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